Excitation transfer and luminescence in porphyrin-carbon nanotube complexes

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Functionalization of carbon nanotubes with hydrosoluble porphyrins (TPPS) is achieved by "π-stacking". The porphyrin/nanotube interaction is studied by means of optical absorption, photo-luminescence and photoluminescence excitation spectroscopies. The main absorption line of the porphyrins adsorbed on nanotubes exhibits a 120 meV red shift, which we ascribe to a flattening of the molecule in order to optimize $\pi - \pi$ interactions. The porphyrin-nanotube complex shows a strong quenching of the TPPS emission while the photoluminescence intensity of the nanotubes is enhanced when the excitation laser is in resonance with the porphyrin absorption band. This reveals an efficient excitation transfer from the TPPS to the carbon nanotube.

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Tailoring the properties of carbon nanotubes by functionalizing their side-wall is one of the key issues towards the realization of carbon nanotube-based optoelectronic or electronic devices. Interactions between nanotubes and porphyrin molecules have attracted much attention for about five years in connection with applications such as nanotubes debundling [1], nanotube sorting [2], photovoltaic cells [3, 4, 5, 6] or biology [7]. Most of the studies deal with either covalent [4, 6] or "π - stacking" [1, 2, 3, 8, 9] functionalization. Changes in the porphyrin optical absorption and emission spectra in the presence of nanotubes have been reported [1, 3, 4, 9] while other studies do not report any changes [2, 8]. Several explanations have been proposed for those changes including porphyrin protonation and H or J-aggregates formation induced by the nanotubes. In contrast and despite the great interest of the question, little work has been devoted to the alteration of nanotubes properties binded to porphyrin molecules.

In this paper, we report on "π-stacking" functionalization of nanotubes with hydrosoluble porphyrins. The interaction between the porphyrin molecules and the nanotubes is studied by optical absorption, photoluminescence and photoluminescence excitation spectroscopies. The Soret band of porphyrins adsorbed on nanotubes exhibits a 120 meV red shift which is interpreted as a consequence of the flattening of the molecule in order to optimize $\pi - \pi$ interactions. A total quenching of the porphyrin fluorescence is observed in the presence of nanotubes. In the same time, the nanotubes photoluminescence is preserved and enhanced when the excitation is tuned in resonance with the Soret band of the "π-stacked" porphyrins. This result clearly reveals an effi-
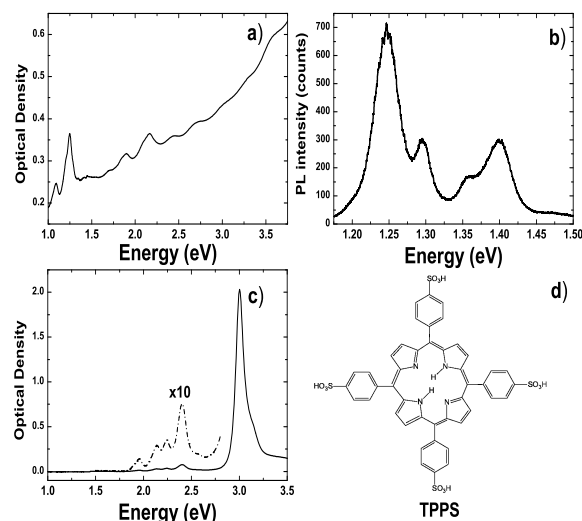

Figure 1: a) Optical absorption of CoMoCat nanotubes embedded in Sodium Dodecyl Sulfate micelles in a pH 8 Normadose buffer. b) Corresponding photoluminescence spectrum of CoMoCat nanotubes embedded in micelles (excitation energy: 2.331 eV). c) Optical absorption of TPPS in a pH 8 Normadose buffer(dashed curve: Q bands contribution rescaled for clarity). d) Chemical structure of TPPS. The phenyl groups are not in the plane of the macrocycle because of the steric hindrance.

cient excitation transfer between the porphyrin molecules and the carbon nanotubes which is an avenue to many applications.

In this study we use CoMoCat carbon nanotubes which are single-wall nanotubes (SWNT) with a mean diameter of about 0.8 nm [10]. The nanotubes are functionalized by using the 5,10,15,20-tetrakis(4-sulfonatophenyl) por-

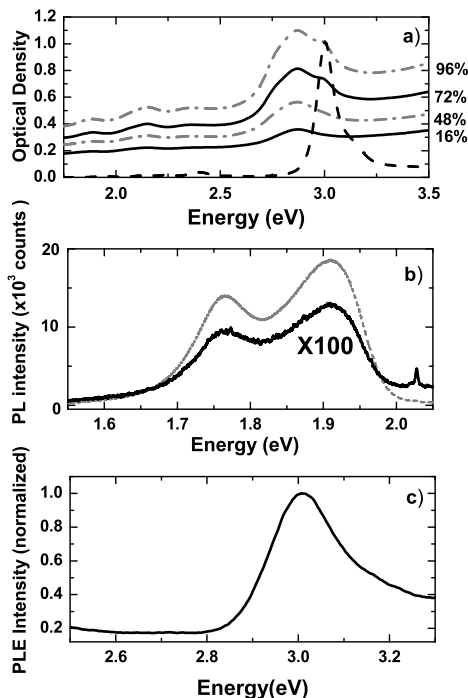*email:lauret@lpqm.ens-cachan.fr, tel: + 33 1 47 40 55 99

Figure 2: a) Optical absorption of TPPS/CoMoCat nanotubes suspensions around the Soret band energy for porphyrin concentrations ranging from 16% to 96%. Free porphyrin (4%) absorption spectrum (black dashed curve) rescaled for clarity. b) Photoluminescence spectra of TPPS (4% [13]) alone (grey) and in the presence of nanotubes (black). c) Photoluminescence excitation spectrum of a porphyrin/nanotube suspension detected at 1.77 eV.

phyrin (TPPS). It was synthesized according to conventional procedures described in the literature [11]. It is soluble in a pH 8 Normadose buffer (10^{-2}M) and its chemical structure is depicted in figure 1d). Nanotubes functionalization is achieved by adding a porphyrin solution (1mg/mL) in a suspension of SWNT (0.1 mg.mL^{-1}) in a pH 8 Normadose buffer. The porphyrin weight fraction is adjusted and increased from 4% (porphyrin/SWNT w/w) up to 96%. After porphyrin addition, the solution is sonicated for 3h with a dismembrator. The sample is placed in a thermostat and cooled in water at 1°C during sonication.

Optical absorption spectra (OAS) are recorded with a spectrophotometer (lambda 900 Perkin-Elmer). Two cw-laser diodes at 3.062 eV (405 nm) and 2.331 eV (532 nm) are used as excitation sources for photoluminescence (PL) experiments. The PL signal is dispersed in a spectrograph (Spectrapro 2500i, Roper Scientific) and detected by a Si CCD camera (Pixis 100B, PI Acton). When detecting in the visible range, photoluminescence excitation experiments (PLE) are performed with a spectrofluorometer (Jobin-Yvon Fluoromax-3), while for de-

tection in the near infrared range a tunable frequency doubled Ti:Saphire laser is used as the excitation source (2.75 eV - 3.1 eV).

The optical absorption spectrum of CoMoCat nanotubes embedded in Sodium Dodecyl Sulfate (SDS) micelles at pH 8 is displayed in figure 1a). The corresponding PL spectrum excited at 2.331 eV is shown in figure 1b). Four main emission bands are observed at 1.24 eV, 1.29 eV, 1.36 eV and 1.40 eV, which are commonly attributed to the (6,5), (8,3), (9,1) and (6,4) nanotubes respectively [10, 12]. The porphyrin optical absorption spectrum is displayed in figure 1c). One can observe the weak Q absorption bands (in the 1.7-2.5 eV range) and the prominent Soret band (at 3 eV). The PL spectrum (grey curve in figure 2b) exhibits two bands at 1.91 eV and 1.77 eV corresponding to singlet-singlet transitions. Note that, once rescaled, the optical absorption spectra of TPPS are identical for concentrations between 4% and 96% [13], showing that porphyrins do not aggregate up to this concentration.

The absorption spectrum of porphyrin/nanotube suspensions is shown in figure 2a) for several porphyrin concentrations. The dashed curve represents the free porphyrin (4%) absorption spectrum rescaled for clarity. For porphyrin concentrations below 72%, the Soret band peaks at 2.88 eV which corresponds to a red shift of 120 meV with respect to the absorption band of free porphyrins. Since we have checked that no aggregation of the porphyrin occurs for these concentrations, we assign this red shift to the interaction between the porphyrin molecules and the nanotubes.

For a concentration of 72% and up, a shoulder appears at 3 eV, which corresponds to the Soret band of free porphyrins. This means that nanotubes no longer bind to porphyrins above this concentration and that additional porphyrins remain free in the suspension. Further experiments are under progress to determine more accurately the saturation threshold. Note that we cannot observe the Q bands of porphyrin/nanotube complexes since the absorption is mainly due to the nanotubes in this energy range (see figures 1a) and 1c)).

Figure 2b) shows the photoluminescence spectra (excited at 3.06 eV) of free porphyrins (4%, grey line) and porphyrin/nanotube complexes (4%, black curve). The latter shows a quenching of 99% of the porphyrin line (around 1.8 eV) indicating a strong interaction between "π-stacked" porphyrins and nanotubes. The photoluminescence excitation spectrum of a porphyrin/nanotube suspension (detection at 1.77 eV) is shown in figure 2c). It peaks at 3 eV, that is at the energy of the Soret band of the free porphyrin. Moreover, after rescaling this spectrum is exactly the same as the one of free porphyrin (not shown here). We conclude that the weak remaining photoluminescence signal of the porphyrins actually arises from residual free porphyrins. As a consequence we deduce that "π-stacked" porphyrins no longer emit

light, supporting the assumption of a strong nanotube-porphyrin interaction.

Several mechanisms may account for the red shift of the Soret band. Protonation of TPPS leads to a red shift of about 140 meV [19]. Since the experiments reported here are performed in a pH 8 buffer and since the TPPS pKa are about 5, protonation of the porphyrin can be ruled out. A red shift of the Soret band may also stem from the formation of J-aggregates [3, 9], which is generally observed in acid environments and leads to a red shift of about 500 meV. We tried to aggregate TPPS in the pH 8 buffer by increasing gradually the porphyrin concentration without any success. In contrast, in an acid medium we were able to form J-aggregates with this protocol, in agreement with previous studies [19]. Thus we deduce that J-aggregates cannot exist in our experimental conditions and therefore cannot account for the observed red shift.

A red shift of the Soret band has also been reported for porphyrins laid on a substrate [20] or self-assembled into nanoparticles [21]. In that case the molecules flatten to enhance the interaction with the substrate or with other porphyrin molecules. The phenyl groups, which make a 90° angle with the plane of the macrocycle for free porphyrins in solution, tend to tilt and to reduce this angle when interacting with the substrate or other molecules. This behavior leads to a red shift of the Soret band of about 200 meV for a tilt of 30° [20]. In our experiments, we assign the observed red shift of the Soret band to a flattening of the porphyrin in contact with a nanotube.

As a consequence, this red shift of the Soret band should depend on the nanotube diameter ; in fact, the larger the nanotube diameter, the more the porphyrin has to flatten in order to optimize the π-π interaction with the nanotube. Thus, the red shift should increase with the tube diameter [20]. Preliminary results show that TPPS adsorbed on nanotubes with a mean diameter of 1.2 nm (synthesized by the electric arc method) exhibit a 170 meV red shift of the Soret band. Compared to the previously mentioned CoMoCat nanotubes, we observe a 40% increase of the red-shift for a 50% increase of the nanotube diameter, which is qualitatively consistent with our interpretation.

Nevertheless, it has been shown that the photoluminescence signal of porphyrins is preserved when they flatten to form nanoparticles [21]. Thus, the strong quenching of the porphyrin fluorescence in the presence of nanotubes cannot be due to the deformation of the molecules. This rather seems to indicate a strong electronic interaction between porphyrins and nanotubes.

Optical absorption and fluorescence were recorded similarly in the spectral range of the nanotube first excitonic transitions usually labelled "S_{11}". The evolution of the nanotube absorption as a function of the porphyrins concentration is depicted in figure 3a). We first observe that
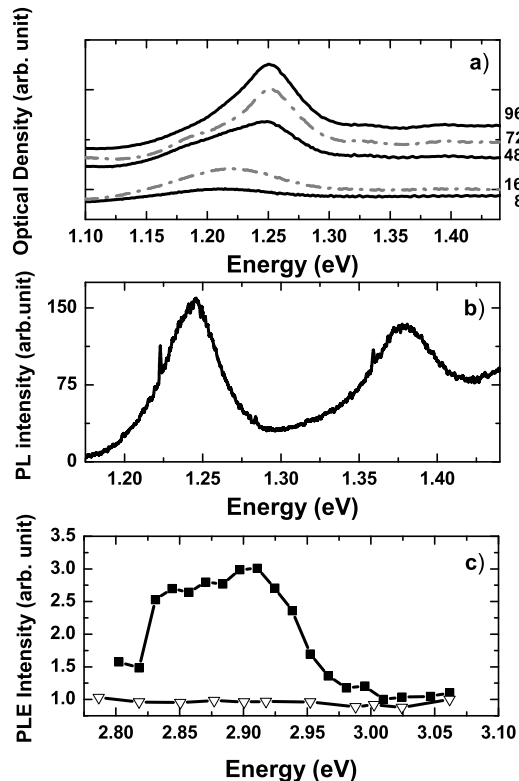

Figure 3: a) Optical density of TPPS/CoMoCat nanotubes suspension around first excitonic transition of nanotubes for different concentrations of porphyrins (from 8% to 96%). Curves have been arbitrary shifted on the Y-axis for clarity. b) Photoluminescence signal of CoMoCat nanotubes in presence of TPPS excited at 2.331 eV. c) Photoluminescence excitation spectra of a porphyrin/nanotube suspension (black squares) and of nanotubes embedded in SDS micelles (open triangles) detected at 1.246 eV.

the specific absorption band of the nanotubes is better resolved when the porphyrin concentration is higher. In order to be more quantitative, we define an aspect ratio "R" such as $R = \frac{OD_{max}}{OD_{min}}$ where OD_{max} is the optical density at the maximum of the band and OD_{min} is the optical density at the high energy foot (1.32 eV) of the band. We get $R = 1.09$ for a porphyrin concentration of 8% and $R = 1.37$ for a concentration of 72%. For comparison, for nanotubes embedded in micelles (reference material, see figure 1a)), we get $R = 1.43$ [14].

The absorption band consists of a shoulder at 1.19 eV and a maximum at 1.251 eV (for TPPS concentration up to 72%). For higher porphyrin concentrations, the shoulder disappears (see the 96% curve in figure 3a)) while the absorption at 1.251 eV increases. This seems to indicate that TPPS interacts preferentially with some specific types of nanotubes (i.e. chiralities).

Further insight can be gained by photoluminescence measurements. Figure 3b) shows the photoluminescence

signal of CoMoCat nanotubes functionalized with TPPS. In contrast to the case of covalent grafting [6], the PL signal of the nanotubes is preserved after functionalization. Transmission electronic microscopy analysis shows that the suspensions contain some individual nanotubes and some remaining bundles. If porphyrins actually foster the debundling of nanotubes, one expects an enhancement of the quantum efficiency for functionalized nanotubes [15, 16, 17, 18]. Indeed, we qualitatively observe that the higher the porphyrin concentration, the larger the nanotubes PL intensity.

The PL signal of functionalized nanotubes exhibits two bands at 1.246 eV and 1.389 eV. Compared to the PL signal of nanotubes embedded in surfactant, two bands -corresponding to (8,3) and (9,1) nanotubes- are missing in the spectrum of functionalized nanotubes. This is consistent with our previous conclusion that a partial nanotube sorting is achieved.

Moreover, the PLE spectrum of porphyrin/nanotube complexes detected at 1.246 eV (see figure 3c)) shows that the PL signal of the functionalized nanotubes is greatly enhanced when the sample is excited at 2.88 eV. In contrast, the PLE spectrum of nanotubes embedded in SDS micelles is flat in this spectral range (see figure 3c)). We assign this PLE band at 2.88 eV to the Soret band of the "π-stacked" porphyrins, as shown from the absorption spectra (see figure 2a)). This clearly means that the PL signal arises from functionalized nanotubes. Furthermore, it shows that light absorbed on "π-stacked" porphyrin states results in a population on excited states of nanotubes. Therefore, it brings evidence for an efficient excitation transfer from the porphyrins to the nanotubes within the "π-stacked" complexes.

In summary, we have demonstrated the functionalization of CoMoCat nanotubes by TPPS porphyrins. Porphyrins "π-stacked" on nanotubes exhibit a red shift of the Soret band, which has been interpreted in terms of a flattening of the porphyrin molecule in order to optimize the $\pi - \pi$ interactions with the nanotube. Moreover, we have shown that TPPS interacts preferentially with some specific classes of nanotubes. In contrast to covalent functionalization, the photoluminescence signal of nanotubes is preserved. In the same time, "π-stacked" porphyrins no longer emit light, but the nanotube fluorescence is enhanced when the excitation energy is tuned in resonance with the absorption band of the porphyrins bringing evidence for a strong excitation transfer from TPPS to the nanotubes. In view of potential applications, the understanding and the optimization of this excitation transfer would be valuable. Time-resolved experiments are under progress to investigate further the electronic states involved in this coupling, as well as its nature and its dynamics.

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